An imidazolium-based organopalladium-functionalized organic–inorganic hybrid silica promotes one-pot tandem Suzuki cross coupling–reduction of haloacetophenones and arylboronic acids

Dacheng Zhang, Tanyu Cheng, Guohua Liu*

Key Laboratory of Resource Chemistry of Ministry of Education, Shanghai Key Laboratory of Rare Earth Functional Materials, Shanghai Normal University, No. 100 Guilin Rd, Shanghai 200234, PR China

ABSTRACT

An imidazolium-based organopalladium-functionalized heterogeneous catalyst is prepared by the immobilization of bis[(diphenylphosphino) ethyltriethoxysilane)]palladium dichloride onto an imidazolium-based organic–inorganic hybrid silica. It enables the one-pot tandem Suzuki cross coupling–reduction of haloacetophenones and arylboronic acids, providing a range of biaryl alcohols with high yields. The superior catalytic performance is attributed to the nature of the uniformly distributive, well-defined confined organopalladium active species within its imidazolium-based silicate network.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Multiple-step organic transformations through an one-pot catalytic process, as an important aspect of green chemistry, have attracted a great deal of interest due to atomic economy and minimum workup [1–5]. However, intrinsic disadvantages of homogeneous organometallic catalysts, such as reuse of expensive organometallic complexes and potential product contamination from leaching of metal, do still hinder their practical applications in industrial process. Thus, development of an immobilized strategy overcomes these barriers is of considerable importance. Silica-based mesoporous materials as supports to immobilize organometallic complexes for catalysis have obtained great achievements [6,7]. In particular, imidazolium-based silica materials as supports have exhibited some salient advantages [8–10]. As a type of environmentally friendly materials, imidazolium-based silica materials possess potential phase transfer function that can promote significantly catalytic efficiency in a biphasic catalysis system [9–10]. Furthermore, functionalized imidazolium-based silica materials can be constructed easily *via* various assembly strategies, [11–14] particularly some materials containing multi-functionality on their silicate networks can realize potentially a multiple-step organic transformation that is still rare in a heterogeneous catalysis. Accordingly, it is reasonable to expect that the construction of an imidazolium-based silica material with multi-functionality in its silicate network has significant benefits for an one-pot multiple-step organic transformation in a heterogeneous catalysis system.

Suzuki cross-coupling reaction of aryl halides and arylboronic acids to biaryls, and catalytic reduction of carbonyls to alcohols are two type of classic organic reactions, which have been investigated extensively both in theoretically and practically [15–17]. Recently, some successful examples through the combination of above two organic reactions to construct biaryl alcohols from reaction of haloacetophenones and arylboronic acids have been explored [18,19]. In both cases, a triazolyl-diylidene-bridged Pd/Ir-complex enables one-pot tandem Suzuki cross-coupling of aryl halides and arylboronic acids followed by reduction to obtain biaryl alcohols, but the transition-metal contamination for reaction product is still unavoidable problem in its practical application. Therefore, the design of a recyclable imidazolium-based silica-supported organopalladium-functionalized heterogeneous catalyst to realize one-pot tandem Suzuki cross coupling–reduction of haloacetophenones and arylboronic acids to prepare a range of biaryl alcohols is highly desirable.

As an effort to develop highly efficient heterogeneous catalysts, [20–25] in this contribution, we utilize the benefits of

an imidazolium-based organic–inorganic hybrid silica (IBOIHS) and develop an organopalladium-functionalized heterogeneous catalyst PdPPh$_2$–IBOIHS (**3**), consisting of uniformly distributive, well-defined confined organopalladium active species within its imidazolium-based silicate network. As expected, the imidazolium functionality and the well-defined confined organopalladium active species within IBOIHS can promote synergistically its catalytic performance. As presented in this study, the heterogeneous catalyst exhibits a high efficiency in the one-pot tandem Suzuki cross coupling–reduction of haloacetophenones and arylboronic acids, providing a range of biaryl alcohols with high yields. Furthermore, the heterogeneous catalyst can be readily recycled and reused repeatedly at least six times without reducing obviously its reactivity.

2. Experimental

Characterization. Pd loading amounts in the catalyst was analyzed using an inductively coupled plasma optical emission spectrometer (ICP, Varian VISTA-MPX). Fourier transform infrared (FT-IR) spectra were collected on a Nicolet Magna 550 spectrometer using KBr method. X-ray powder diffraction (XRD) was carried out on a Rigaku D/Max-RB diffractometer with CuKα radiation. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6380LV microscope operating at 20 kV. Transmission electron microscopy (TEM) images were performed on a JEOL JEM 2010 electron microscope at an acceleration voltage of 220 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Perkin-Elmer PHI 5000C ESCA system. All the binding energies were calibrated by using the contaminant carbon (C_{1s} = 284.6 eV) as a reference. Nitrogen adsorption isotherms were measured at 77 K with a Quantachrome Nova 4000 analyzer. The samples were measured after being outgassed at 423 K overnight. Pore size distributions were calculated by using the BJH model. The specific surface areas (S_{BET}) of samples were determined from the linear parts of BET plots (p/p_0 = 0.05–1.00). Solid-state ^{13}C (100.5 MHz), ^{29}Si (79.4 MHz) and ^{31}P (169.3 MHz) CP/MAS NMR were obtained on a Bruker DRX-400 spectrometer.

Preparation of PdPPh$_2$–IBOIHS (3). A typical procedure was as follows: under argon atmosphere, to a stirred suspension of IBOIHS (**1**) (1.0 g) in 20.0 mL of dry toluene was added a solution of PdCl$_2$[PPh$_2$(CH$_2$)$_2$Si(OEt)$_3$]$_2$ (**2**) (0.19 g, 0.20 mmol) in 5.0 mL of dry toluene at room temperature. The resulting mixture was refluxed for 24 h. After cooling to room temperature, the volatiles were removed in vacuum and 50 mL of water was added. Then the residues were filtrated and washed twice with 50 mL of water and 50 mL of CH$_2$Cl$_2$. After Soxhlet extraction in dry CH$_2$Cl$_2$ to remove homogeneous and unreacted start materials, the solid was dried under reduced pressure overnight to afford the catalyst (**3**) (1.08 g) as a brown powder. ICP analysis showed that the Pd loading-amount was 8.48 mg (0.08 mmol) per gram catalyst. IR (KBr) cm^{-1}: 3430.5 (s), 3148.0 (w), 3095.1 (w), 2934.5 (w), 1634.9 (w), 1565.7 (m), 1448.9 (w), 1411.3 (w), 1351.9 (w), 1245.5 (w), 1132.4 (s), 1051.2 (s), 921.7 (m), 762.9 (w), 702.2 (w), 478.8 (w); ^{13}C CP/MAS (100.5 MHz): 9.4 (Si$\underline{C}$H$_2$CH$_2$CH$_2$N), 23.9 (SiCH$_2$$\underline{C}H_2CH_2$N), 28.3, 19.2 (P$\underline{C}H_2$), 51.7 (SiCH$_2CH_2$$\underline{C}H_2$N), 123.0 ($\underline{C}$H of imidazolium) 129.1 ($\underline{C}$H-Ph), 135.8 ($\underline{C}$H of imidazolium) ppm; ^{29}Si MAS/NMR (79.4 MHz): T^1 (δ = − 50.9 ppm), T^2 (δ = − 59.5 ppm), T^3 (δ = − 69.0 ppm); ^{31}P CP/MAS (169.3 MHz): 10.4 ppm.

General procedure for one-pot tandem reactions. A typical procedure was as follows. Catalyst **3** (25.00 mg, 2.00 μmol of Pd based on ICP analysis), ketones (0.10 mmol), and arylboronic acid (0.12 mmol), NaOH (12.0 mg, 0.30 mmol) and 4.0 mL i-PrOH were added sequentially to a 10.0 mL round-bottom flask. The mixture was then stirred at 82 °C for 12 h. During this period, the reaction

was monitored constantly by TLC. After completion of the reaction, the catalyst was separated by centrifugation (10,000 rpm) for the recycling experiment. The aqueous solution was extracted with ethyl ether (3 × 3.0 mL). The combined ethyl ether extracts were washed with brine twice and then dehydrated with Na$_2$SO$_4$. After evaporation of ethyl ether, the residue was purified by silica gel flash column chromatography to afford the desired products.

3. Results and discussion

3.1. Synthesis and structural characterization of the heterogeneous catalyst 3

The organopalladium-functionalized heterogeneous catalyst, abbreviated as PdPPh$_2$–IBOIHS (**3**) [PdPPh$_2$: [26,27]], was prepared as outlined in Scheme 1. Firstly, the imidazolium-based IBOIHS (**1**) was synthesized *via* the hydrolysis–condensation of 1,3-bis(3-(triethoxysilyl)propyl)-1 *H*-imidazol-3-ium iodide according to the reported method [28,29]. The directly postgrafting bis[(diphenylphosphino) ethyltriethoxysilane)]palladium dichloride (**2**) onto IBOIHS did then afford the rude PdPPh$_2$-functionalized IBOIHS. Finally, the pure catalyst **3** was obtained successfully by thoroughly Soxhlet extraction to clean of rude catalyst, obtaining its pure form as a brown powder (see SI in Figs. S1–S4).

Incorporation of well-defined site-single PdPPh$_2$-functionality within its IBOIHS silicate network could be proven by solid-state ^{13}C cross-polarization (CP)/magic angle spinning (MAS) NMR spectroscopy. As shown in Fig. 1, catalyst **3** produced strong carbon signals of Si$\underline{C}$H$_2$$\underline{C}H_2$$\underline{C}H_2$N (at 9.4, 23.9 and 51.7 ppm) and of N$\underline{C}$H$\underline{C}$HN$\underline{C}$HN groups (at 123.0 and 135.8 ppm), corresponding to the propyl and imidazolium moiety as the IBOIHS main network. Characteristic carbon atoms of −$\underline{C}$H$_2$P$\underline{C}$$_6H_5$ groups in catalyst **3** could be observed clearly at 28.3, 129.1 ppm that were marked in its spectrum, respectively. These peaks were absent in the spectrum of **1**, suggesting the successful incorporation **2** in its IBOIHS silicate network. Chemical shifts of **3** were strongly similar to those of its homogeneous counterpart **2** (see SI in Fig. S2), demonstrating that both had the same well-defined single-site active species that could be further confirmed by ^{31}P CP MAS spectra (see SI in Fig. S3) [26]. In addition, its solid-state ^{29}Si MAS NMR spectrum further revealed its organosilicate network as shown in Fig. 2. It was found that catalyst **3** produced one group of exclusive *T* signals derived from organosilica, suggesting that all Si species were covalently attached to carbon atoms [30,31]. Strong *T*
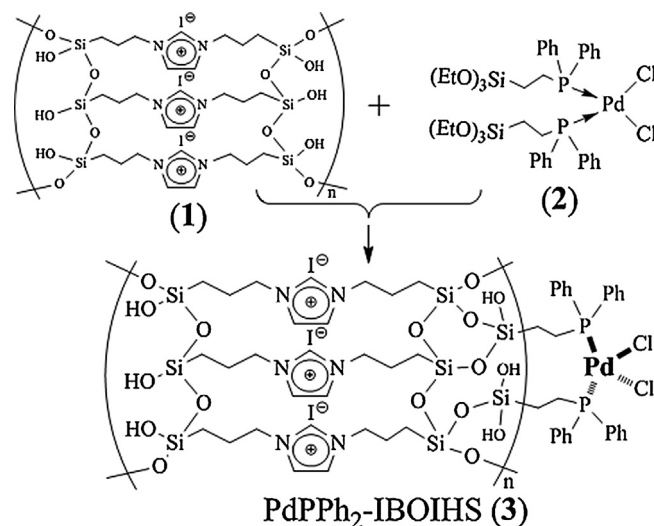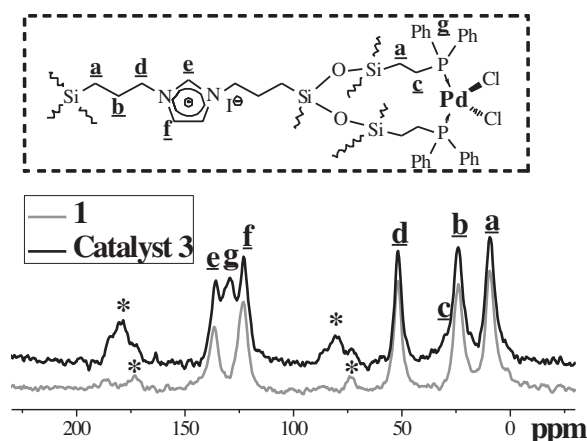

Scheme 1. Preparation of the heterogeneous catalysts.

Fig. 1. ^{13}C CP MAS NMR spectra of the IBOIHS (**1**) and catalyst **3**.

signals at −59.5 and −69.0 ppm in the spectrum of **3** are attributed to T^2(R–Si(OSi)$_2$(OH)] and T^3(R–Si(OSi)$_3$) (R = propyl or ethyl-linked groups) when were compared with those typical isomer shift values in the literature [26] (−48.5, −58.5, and −67.5 ppm for T^1–T^3 of [R(HO)$_2$SiOSi], [R(HO)Si(OSi)$_2$], and [RSi(OSi)$_3$], respectively). This observation demonstrated that catalyst **3** possessed organosilicate network with R–Si(OSi)$_2$(OH) and R–Si(OSi)$_3$ species as its main silicate walls.

Furthermore, the absence of signals for Q-series from −90 to −120 ppm indicated that the carbon−silicon bond was not cleaved during the hydrolysis–condensation process. Furthermore, the nitrogen adsorption–desorption isotherms (Fig. S4) disclosed that catalyst **3** was mesoporous due to the sharp adsorption step at higher relative pressure values (0.60–0.98) with a very narrow H1 hysteresis loop [32] while the TEM image and TEM with a chemical mapping technique indicated that catalyst **3** was composed of micrometer particles and the palladium centers were uniformly distributive within its nanostructure (Fig. 3, also see the enlarged SEM and TEM in SI in Fig. S5).

3.2. Catalytic property of the heterogeneous catalyst 3

On the basis of the obtained heterogeneous catalyst **3**, the Suzuki cross-coupling of 4-iodoacetophenone and phenylboronic acid to 1-(biphenyl-4-yl) ethanone, followed by the reduction of 1-(biphenyl-4-yl) ethanone to 1-(biphenyl-4-yl) ethanol were investigated at first [18–19,33–36,33–39]. According to the reported method [18], several bases were screened based on the same reaction solvent and reaction temperature in the literature. As shown in Table 1, it was found that the one-pot tandem Suzuki coupling–reduction reactions with weak bases including Cs$_2$CO$_3$, K$_2$CO$_3$, Na$_2$CO$_3$, K$_2$PO$_4$ and KF only afforded the side-products of Suzuki cross-coupling. No reductive products could be observed
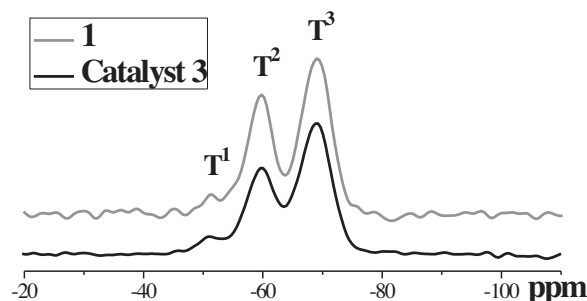

Fig. 2. ^{29}Si CP MAS NMR spectra of the IBOIHS (**1**) and catalyst **3**.
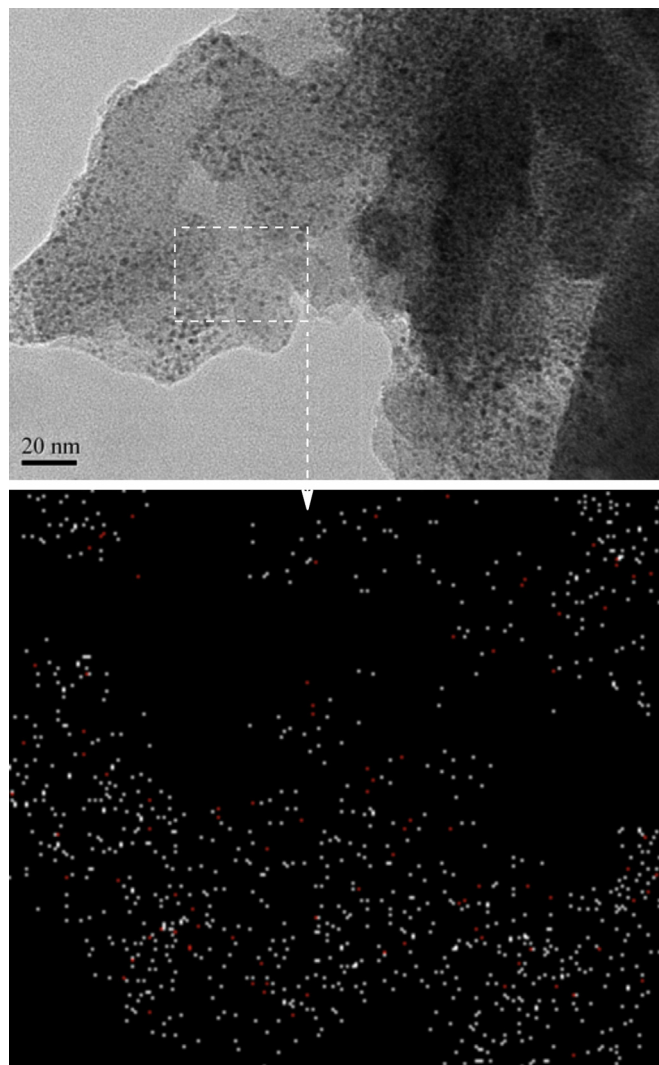

Fig. 3. (a) TEM image of **3** and (b) TEM image with a chemical mapping of **3** showing the distribution of Pd (red) and Si (white). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

in these cases (entries 1–5). Whilst the reactions with the strong basic conditions, the one-pot tandem Suzuki coupling–reduction reactions enabled to transfer 1-(biphenyl-4-yl) ethanone to 1-(biphenyl-4-yl) ethanol from the reaction of 4-iodoacetophenone and phenylboronic acid, but the reactions with *t*-BuOK and KOH as bases afforded a mixture of 1-(biphenyl-4-yl) ethanone and 1-(biphenyl-4-yl) ethanol (entries 6–7). Interestingly, only in the case of NaOH as a base, the reaction could give the clean product of 1-(biphenyl-4-yl) ethanol with 99% yield (entry 8), which only tiny biphenyl produced *via* the self-coupling of phenylboronic acid were observed due to the slightly excess phenylboronic acid. Furthermore, the optimization of substrate-to-catalyst mole ratio disclosed 2.0 mol% of **3** as catalyst is the optimal amount of heterogeneous catalyst (entries 8–10). As a result, the one-pot tandem Suzuki coupling–reduction reaction with 2.0 mmol% **3** as a catalyst, NaOH as a base, *i*-PrOH as a hydrogen resource and solvent at 82 °C was determined as an optimal reaction condition.

Based on the clean one-pot tandem Suzuki coupling–reduction reaction in above optimal reaction condition, it provided an opportunity to investigate its reaction time course from the reaction of 4-iodoacetophenone and phenylboronic acid catalyzed by catalyst **3**. As shown in Fig. 4, it was found that the Pd-catalyzed Suzuki cross-coupling of 4-iodophenylethanol and phenylboronic

Table 1
Optimization of reaction condition in the tandem Suzuki-coupling/transfer hydrogenation of 4-iodoacetophenone and phenylboronic acid.[a]
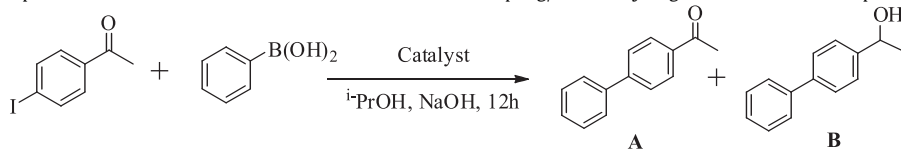
Entry	Base	Yield A (%)[b]	Yield B (%)[b]
1	Cs_2CO_3	99	nd
2	K_2CO_3	97	nd
3	Na_2CO_3	55	nd
4	K_3PO_4	95	nd
5	KF	66	nd
6	t-BuOK	35	65
7	KOH	22	78
8	NaOH	Trace	99
9	NaOH	Trace	95[c]
10	NaOH	Trace	99 [d]

[a] Reaction conditions: catalyst **3** (25.00 mg, 2.00 μmol of Pd based on the ICP analysis), base (0.30 mmol), 4-iodoacetophenone (0.10 mmol), phenylboronic acid (0.12 mmol), and 4.0 mL of 2-propanol, reaction temperature (82 °C), reaction time 12 h.

[b] Determined by ^{1}H-NMR spectra.

[c] Data were obtained using 1.8 mol% of catalyst **3**.

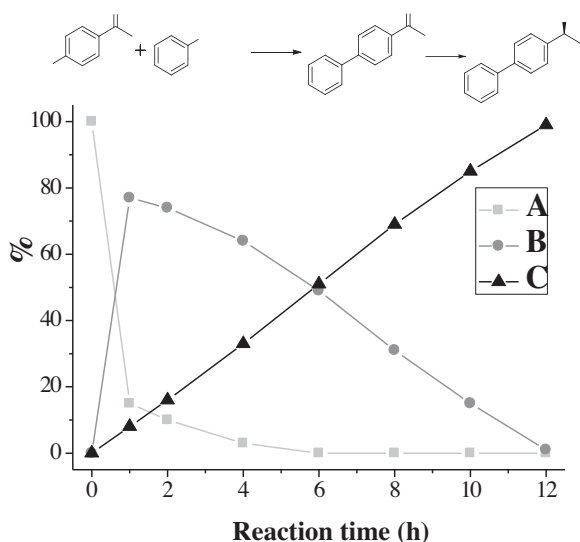[d] Data were obtained using 2.2 mol% of catalyst **3**.

Fig. 4. Time course of the transformation of 4-iodoacetophenone and phenylboronic acid with catalyst **3** (reactions were carried out at 82 °C at substrate-to-catalyst mole ratio of 50 in 4.0 mL of 2-propanol).

acid processes at first, which is fast as seen by the formation of 1-(biphenyl-4-yl) ethanone (B) in a maximum conversion of 77% after 1.0 h of reaction. Subsequently, the reduction of 1-(biphenyl-4-yl) ethanone occurs smoothly with 2-propanol as a hydrogen resource, providing the target product of 1-(biphenyl-4-yl) ethanol (C). This behavior is obviously differed from that observed in our previous report, in which one-pot tandem Suzuki coupling–reduction reaction with the reduction at first, and then followed by Suzuki cross-coupling reaction [25]. Therefore, the different reaction sequence disclosed the inherent role of different reaction conditions in a similar tandem reaction.

Having established that catalyst **3** enabled to catalyze steadily the Suzuki cross-coupling reaction followed by transfer hydrogenation reaction of 4-iodoacetophenone and phenylboronic acid to give the clean 1-(biphenyl-4-yl) ethanol, we further investigated its general applications in the one-pot tandem Suzuki coupling–reduction reactions with different arylboronic acids. As shown in Table 2, in general, a variety of arylboronic acids were smoothly reacted with 4-iodoacetophenone to afford the clean

products in desirable yields (entries 3–8). Notably, high catalytic performance should be due to the well-defined single-site organopalladium catalytic nature validated by its ^{13}C CP/MAS NMR. Further, evidence supporting this view came from an X-ray photoelectron spectroscopy (XPS) investigation. As shown in Fig. 5, XPS investigation showed that catalysts **3** had the similar Pd 3d$^{5/2}$ electron binding energy to its homogenous counterpart **2** (337.61 versus 337.62 eV). This observation demonstrated that catalyst **3** retained the original coordinated environment of its homogeneous counterpart **2**. In addition, it was also found that the one-pot tandem Suzuki coupling–reduction reaction of 4-bromoacetophenone and phenylboronic acid could afford the products with desirable yield (entry 2). Interestingly, the one-pot tandem Suzuki cross coupling–reduction could also be used toward the synthesis of biaryldiols, in which the reaction of 4-iodoacetophenone and (4-acetylphenyl) boronic acid afforded a 1,1′-([1,1′-biphenyl]-4,4′-diyl) diethanol in 99% yield (entry 9).

It is noteworthy that this one-pot tandem reaction catalyzed by catalyst **3** presented higher yield than that of its homogeneous counterpart **2** (entry 1 versus entry 1 in bracket), suggesting the uniformly distributive palladium species within the imidazolium-based silicate network in catalyst **3** could promote efficiently catalytic performance. To gain better insight into the role of the uniformly distributive palladium species during the catalytic process and the nature of imidazolium-functionality within IBOIHS network, a kinetic profile of the tandem Suzuki cross coupling–reduction of 4-iodoacetophenone and phenylboronic acid catalyzed by **3**, by its homogeneous counterpart **2**, and by the mixed IBOIHS (**1**) and **2** were investigated. As shown in Fig. 6, it was found that the initial TOF values of **3**, the mixed IBOIHS (**1**) plus **2**, and **2** were 4.0, 2.5 and 1.5 mol/(mol h), respectively. As observed, the reactivity with the mixed IBOIHS (**1**) and **2** as a catalyst was higher than that obtained with **2**, disclosing the function of imidazolium-functionality. Meanwhile, the reactivity with **3** as a catalyst had more than twice increase of reaction rate relative to **2**, suggesting both benefits of function of imidazolium-functionality and of uniformly distributive organopalladium-functionality within organic–inorganic hybrid silica. These observations confirmed that the enhanced catalytic efficiency in the one-pot tandem Suzuki cross coupling–reductions catalyzed by **3** ascribed the synergistic role of the imidazolium-functionality and the uniformly distributive confined organopalladium active species within its silicate

Table 2
Tandem Suzuki-coupling/transfer hydrogenation of haloacetophenones and arylboronic acids.[a]
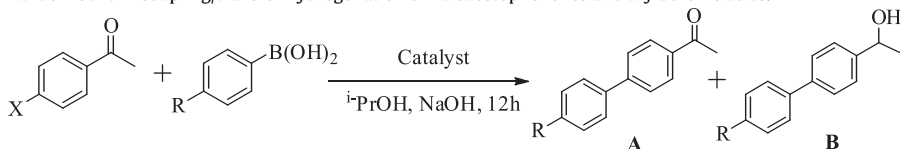
Entry	X	R	Yield A (%)[b]	Yield B (%)[b]
1	I	H	nd (20)[c]	99 (80)[c]
2	Br	H	Trace	94
3	I	4-F	Trace	85
4	I	4-Cl	Trace	90
5	I	4-OCH$_3$	Trace	92
6	I	4-CF$_3$	Trace	98
7	I	4-NO$_2$	nd	99
8	I	4-CN	nd	99
9	I	4-COCH$_3$	nd	99

[a] Reaction conditions: catalyst **3** (25.0 mg, 2.0 mol%, 2.00 μmol of Pd based on the ICP analysis), NaOH (0.30 mmol), 4-haloacetophenone (0.10 mmol), arylboronic acids (0.12 mmol), and 4.0 mL of 2-propanol, reaction temperature (82 °C), reaction time 12 h.

[b] Determined by ^{1}H-NMR spectra (see SI in Fig. S8).

[c] Data in the bracket were obtained using its homogenous counterpart **2** as a catalyst.
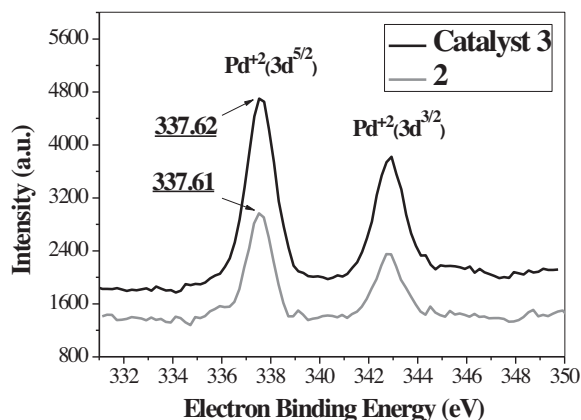

Fig. 5. XPS spectra of catalyst **3** and its homogeneous counterpart **2**.

network validated by its ^{13}C CP/MAS NMR and its SEM investigation.

An important feature in design of any heterogeneous catalyst is that that catalyst could be recovered and the recycled catalyst still retains its reactivity after multiple cycles. Remarkably, catalyst **3** was recovered easily and reused repeatedly when one-pot tandem Suzuki cross coupling–reduction of 4-iodoacetophenone and phenylboronic acid was chosen as a model reaction. It was found that, in six consecutive reactions, the recycled catalyst **3** did still afford the desirable product with 95% yield (see SI in Table S1). However, the reactivity of the recycled catalyst **3** dropped sharply in seventh run, where only 76% yield could be obtained. In order to explore the nature of the deactivation of the recycled catalyst **3**, the TEM image and XPS spectrum after the 7th run were further investigated (Figs. S6–S7). The TEM image of the recycled catalyst **3** showed that the palladium-functionality was still dispersed and no obvious aggregation onto IBOIHS silicate network could be observed (Fig. S6), suggesting that the deactivation of the recycled catalyst **3** came possibly from the other factors rather than the aggregations of palladium species. The XPS data disclosed clearly that the recycled catalyst **3** contained the mixed organopalladium complex (Pd^{+2}) and palladium nanoparticle (Pd^0) onto its IBOIHS silicate network (about 69% of Pd^{2+} species and 31% of Pd^0 species) (Fig. S7), indicating the the deactivation of the recycled catalyst **3** may be ascribed the leaches of non-covalent absorption of Pd^0 species onto the IBOIHS silicate network. The evidence

supported this view coming from the ICP–MS analysis, where the amount of Pd after the 7th run was 6.89 mg (0.0658 mmol) per gram of catalyst and 18.8% of Pd was lost relative to the starting amount of the fresh catalyst **3**. Therefore, these observations suggest that the mechanism of deactivation of the recycled catalyst **3** involves the formation of a large number of Pd^0 nanoparticles, which leads to Pd-leaches from the supported IBOIHS silicate network due to their non-covalent physical absorption interactions. Also, in order to explore its recyclability, another attempt through a continuous-flow synthesis was investigated as shown in Fig. 7 [40]. In this case, 4-iodoacetophenone (1.00 mmol) and phenylboronic acid (1.20 mmol) completely dissolved in a diluted aqueous solution of sodium hydroxide in *i*-PrOH (20 mL), while the X-Cube (ThalesNano) instrument was equipped with the packed bed reactor containing the heterogeneous catalyst **3** (500 mg of catalyst was filled this bed reactor, 0.6 mL volume, 70 mm × 4 mm). The reaction parameters/temperature (80 °C), 0.1 mL/min flow rate were selected on the flow reactor, and processing was started, whereby only a diluted aqueous solution of sodium hydroxide in *i*-PrOH without 4-iodoacetophenone and phenylboronic acid was pumped through the system until the instrument had achieved the desired reaction parameters and stable processing was assured. During the desired reaction parameters and stable processing was observed, the freshly prepared reaction mixture was pumped. After
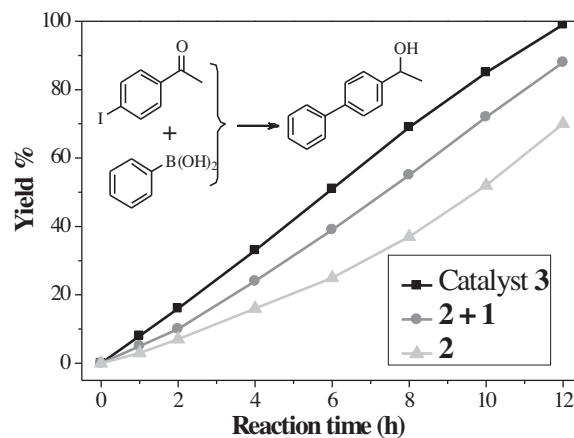

Fig. 6. Comparison of tandem reaction catalyzed by catalyst **3**, its homogeneous counterpart **2**, and the mixed IBOIHS (**1**) and **2**. Reactions were carried out at 82 °C at substrate-to-catalyst mole ratio of 50 in 4.0 mL of 2-propanol.
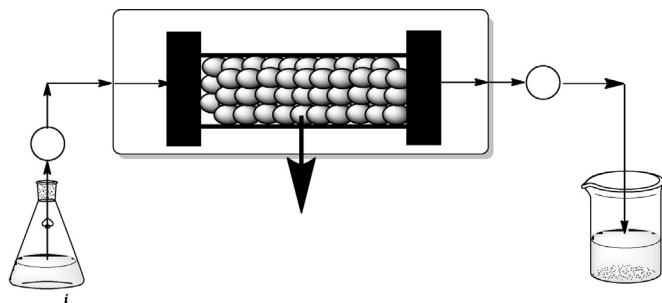
Fig. 7. Schematic of continuous flow process for the tandem Suzuki-coupling/transfer hydrogenation of 4-iodoacetophenone and phenylboronic acid.

processing through the flow reactor, the product was obtained. The result showed that the product of 1-(biphenyl-4-yl) ethanol in a 91% yield with respect to 4-iodoacetophenone was obtained, which offer a potential application in an industrial interest.

4. Conclusions

In conclusion, we take advantage of benefit of imidazolium-functionality to develop an imidazolium-based organopalladium-functionalized organic–inorganic hybrid silica. As a heterogeneous catalyst, it catalyzes efficiently the one-pot tandem Suzuki cross coupling–reduction of haloacetophenones and arylboronic acids to prepare biaryl alcohols, which is better than its homogeneous counterpart in catalytic performance. As demonstrated in this study, the high catalytic performance in the one-pot process is attributed to the uniformly distributive, well-defined confined organopalladium active species within the imidazolium-based silicate network. Furthermore, the heterogeneous catalyst **3** could be recovered conveniently and subsequently reused at least 6 times without affecting its reactivity, showing a promising potential in practical organic synthesis.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2015.03.024.

References

[1] L. Tietze, G. Brasche, K. Gericke, Domino Reactions in Organic Synthesis, Wiley-VCH, Weinheim, 2006.
[2] G. Posner, Chem. Rev. 86 (1986) 831.
[3] C. Grondal, M. Jeanty, D. Enders, Nat. Chem. 2 (2010) 167.
[4] L. Albrecht, H. Jiang, K. Jørgensen, Angew. Chem. Int. Ed. 50 (2011) 8492.
[5] C. Vaxelaire, P. Winter, M. Christmann, Angew. Chem. Int. Ed. 50 (2011) 3605.
[6] F. Kleitz, Handbook of Asymmetric Heterogeneous Catalysis, Wiley-VCH, Weinheim, 2008, pp. 178.
[7] H. Zou, S. Wu, J. Shen, Chem. Rev. 108 (2008) 3893.
[8] J. Dupont, R. de Souza, P. Suarez, Chem. Rev. 102 (2002) 3667.
[9] B. Karimi, M. Gholinejad, M. Khorasani, Chem. Commun. 48 (2012) 8961.
[10] B. Karimi, D. Elhamifar, O. Yari, M. Khorasani, H. Vali, J. Clark, A. Hunt, Chem. Eur. J. 18 (2012) 13520.
[11] P. Borah, X. Ma, K. Nguyen, Y. Zhao, Angew. Chem. Int. Ed. 51 (2012) 7756.
[12] M. Waki, N. Mizoshita, T. Tani, S. Inagaki, Angew. Chem. Int. Ed. 50 (2011) 11667.
[13] M. Guan, W. Wang, E. Henderson, Ö. Dag, C. Kübel, V. Chakravadhanula, J. Rinck, I. Moudrakovski, J. Thomson, J. McDowell, A. Powell, H. Zhang, G. Ozin, J. Am. Chem. Soc. 134 (2012) 8439.
[14] M. Mandal, M. Kruk, Chem. Mater. 24 (2012) 123.
[15] A. Suzuki, Pure Appl. Chem. 57 (1985) 1749.
[16] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457.
[17] R. Malacea, R. Poli, E. Manoury, Coord. Chem. Rev. 254 (2010) 729.
[18] A. Zanardi, J. Mata, E. Peris, J. Am. Chem. Soc. 131 (2009) 14531.
[19] S. Gonell, M. Poyatos, J. Mata, E. Peris, Organometallics 31 (2012) 5606.
[20] W. Xiao, R. Jin, T. Cheng, D. Xia, H. Yao, F. Gao, B. Deng, G. Liu, Chem. Commun. 48 (2012) 11898.
[21] D. Xia, T. Cheng, W. Xiao, K. Liu, Z. Wang, G. Liu, H. Li, W. Wang, ChemCatChem 5 (2013) 1784.
[22] R. Liu, R. Jin, L. Kong, J. Wang, C. Chen, T. Cheng, G. Liu, Chem. Asian J. 8 (2013) 3108.
[23] G. Liu, J. Wang, T. Huang, X. Liang, Y. Zhang, H. Li, J. Mater. Chem. 20 (2010) 1970.
[24] D. Zhang, X. Gao, T. Cheng, G. Liu, Sci. Rep. 4 (2014) 5091.
[25] D. Zhang, J. Xu, Q. Zhao, T. Cheng, G. Liu, ChemCatChem 6 (2014) 2998.
[26] O. Kröcher, O. Köppel, M. Fröba, A. Baiker, J. Catal. 178 (1998) 284.
[27] N. Linares, A. Sepúlveda, M. Pacheco, J. Berenguer, E. Lalinde, C. Nájera, J. Garcia-Martinez, New J. Chem. 35 (2011) 225.
[28] V. Polshettiwar, R. Varma, Tetrahedron 64 (2008) 4637.
[29] B. Karimi, A. Maleki, D. Elhamifar, J. Clark, A. Hunt, Chem. Commun. 46 (2010) 6947.
[30] S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, Nature 416 (2002) 304.
[31] X. Yang, F. Zhu, J. Huang, F. Zhang, H. Li, Chem. Mater. 21 (2009) 4925.
[32] F. Fakhfakh, L. Baraket, A. Ghorbel, J.M. Fraile, C. Herrerías, J. Mayoral, J. Mol. Catal. A: Chem. 329 (2010) 21.
[33] E. Burda, W. Hummel, H. Gröger, Angew. Chem. Int. Ed. 47 (2008) 9551.
[34] V. Gauchot, W. Kroutil, A. Schmitzer, Chem. Eur. J. 16 (2010) 6748.
[35] E. Burda, W. Bauer, W. Hummel, H. Gröger, ChemCatChem 2 (2010) 67.
[36] A. Prastaro, P. Ceci, E. Chiancone, A. Boffi, R. Cirilli, M. Colone, G. Fabrizi, A. Stringaroe, S. Cacchi, Green Chem. 11 (2009) 1929.
[37] A.R. Siamaki, A.E.R.S. Khder, V. Abdelsayed, M.S. El-Shall, B.F. Gupton, J. Catal. 279 (2011) 1.
[38] H.A. Elazab, A.R. Siamaki, S. Moussa, F. Gupton, M.S. El-Shall, Appl. Catal. A. 491 (2015) 58.
[39] F. Zhang, C. Kang, Y. Wei, H. Li, Adv. Funct. Mater. 21 (2011) 3189.
[40] I.I. Junior, M.C. Flores, F.K. Sutili, S.G.F. Leite, L.S. de, M. Miranda, I.C.R. Leal, R.O.M.A. de Souza, Org. Process Res. Dev. 16 (2012) 1098.